

A STUDY OF THE ADSORPTION OF H_2O ON SILICA GEL

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

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LEONARD H. COHAN

BALTIMORE
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THE RATE OF SORPTION OF WATER VAPOR ON SILICA GEL AND IRON-SILICA GEL¹

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INTRODUCTION

The time necessary for attaining equilibrium in the sorption of water by silica gel, charcoal, etc., has been reported as anywhere from three hours or less (7) up to several months (2). The more rapid sorption rates were found in the absence of permanent gases. Thus the retarding of the diffusion of water vapor by air or other permanent gas present in the apparatus may be sufficient explanation for this enormous difference in rates. However, certain other experiments in the literature indicate that the difference in rates may be due to a more specific effect depending on an interaction of the gas present with the sorbent and even with the sorbate (the substance being sorbed). For example, Burrage (3) found that carbon tetrachloride was taken up almost instantaneously by charcoal, provided that permanent gases (particularly oxygen) were rigidly excluded. Allmand, Burrage, and Chaplin (2) attributed a slow rate of adsorption of various vapors on charcoal to oxygen which probably covers the active centers of the charcoal. Frankenburger and Hodler (5) found, likewise, that minute traces of oxygen hindered the adsorption of hydrogen on tungsten. Furthermore, Patrick and Opdycke (24), using a dynamic sorption method, the vapor being carried in an air stream, found that equilibrium was established rapidly with all vapors studied except water. This last experiment points—at least in the presence of air—to a fundamental difference between the rate of sorption of water and that of other vapors. Since water behaves uniquely, also, with respect to the phenomenon of sorption hysteresis,² it is possible that considerable light may be

¹ A brief summary of the work submitted to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

² Sufficient care (removal of impurities and foreign gases) enables one to eliminate hysteresis in the sorption on silica gel of all vapors except water. In only two (references 6 and 13) of the scores of investigations made has hysteresis been reported as eliminated in the case of water on silica gel. Unpublished investigations of one of the authors (4) has always shown hysteresis.

thrown on sorption phenomena in general by a closer examination of the sorption rate (in the presence and in the absence of permanent gases) of water on a sorbent such as silica gel.

The contention that traces of permanent gas have a marked effect on the rate of sorption appears frequently in the literature. The following work was undertaken in order to examine the validity of this contention in the case of the sorption of water vapor by gels.

EXPERIMENTAL

The silica gel used was a commercial sample carefully purified by refluxing with concentrated nitric acid and then washing with distilled water. After first activating the gel by heating in a current of dry air to 300–400°C. for twelve hours, a sample weighing 0.597 g. was placed in the apparatus and evacuated to 10^{-6} mm. at 200–250°C.

The iron-silica gel was prepared according to the method of Klosky and Patrick (8). To 200 cc. of a 1.25 per cent sodium silicate (commercial) solution was added 100 cc. of a 5.2 per cent ferric chloride solution. The silicate solution was stirred mechanically during the addition. The solution gelled nicely in about fifteen minutes; syneresis began within twenty-four hours. The resulting gel was freed from dissolved salts by dialysis and activated. The activation was accomplished by evacuating to 10^{-6} mm. at 150–200°C. The sample weighed 0.716 g.

Distilled water was used. In the experiment carried out in the absence of permanent gases, the pressure of gas in equilibrium with the water was reduced to 10^{-4} mm. The vapor pressure of the water was kept at 4.6 mm. by surrounding the tube containing the water with a bath of ice and water.

The gases used (hydrogen, nitrogen, oxygen, and air) were dried; the first two were freed from oxygen.

A quartz-spiral sorption balance, described by McBain and Bakr (11), was used, and permitted the amount of water sorbed to be determined without withdrawing the sample from the apparatus. The extension of the spiral was read with a cathetometer to an accuracy corresponding to ± 0.3 mg. An air thermostat regulated the temperature of the tube containing the spiral and gel to $\pm 0.1^\circ\text{C}.$, the vapor pressure corresponding to this temperature being taken from the International Critical Tables.

A vacuum of 10^{-6} mm. or better could be attained in the apparatus by means of a two-stage mercury-vapor pump backed by an oil pump. However, no attempt was made to exclude mercury vapor.

RESULTS AND DISCUSSION

The first series of measurements (adsorption of water and silica gel, figure 1) shows that the rate of adsorption is independent of the pressure of air present, over the range 4×10^{-4} mm. to 0.5 mm. The pressure of

water vapor was 4.6 mm.; the temperature of the gel 25°C. Similar results were obtained with the gel at 23°C. The amount of water adsorbed, a (in grams of water sorbed per hundred grams of dry gel), is plotted against the time, t , in minutes. a is only that water in excess of whatever water is contained in the "dry gel". By "dry gel" we mean the gel in equilibrium

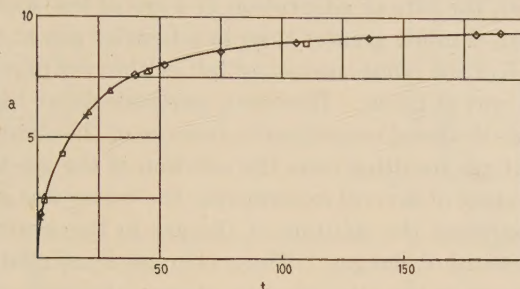


FIG. 1. Adsorption on silica gel in the absence of permanent gases. Ordinate: amount of water adsorbed, a , in grams per 100 grams of dry gel. Abscissa: time, t , in minutes. Vapor pressure of water, 4.6 mm. Temperature of gel, 25°C. Pressure of air: $\square$, 2.4×10^{-4} mm.; $\times$, 4×10^{-4} mm.; $\odot$, 10^{-2} mm.; $\triangle$, 2.6×10^{-1} mm.; $\diamond$, 5×10^{-1} mm.

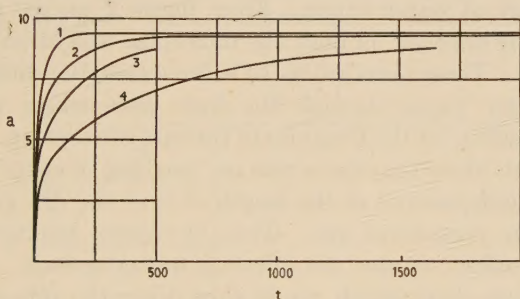


FIG. 2. Adsorption on silica gel in the presence of gases. Ordinate: a in grams per 100 grams of gel. Abscissa: time, t , in minutes. Vapor pressure of water, 4.6 mm. Temperature of gel, 25°C. Curve 1, copied from figure 1, shows rate of adsorption in absence of gases. Curve 2 shows rate of adsorption in the presence of air, nitrogen, or oxygen at an average pressure of 1 mm. Curve 3 shows rate of adsorption in the presence of hydrogen at 3.9 mm. Curve 4 shows rate of adsorption in the presence of air, nitrogen, or oxygen at 3.6 mm.

with a vacuum of 10^{-6} mm. at 25°C. Under these conditions the gel actually contained about 4.9 per cent water. In order not to confuse the figures, only a few of the points obtained are recorded.³

³ The curve of figure 1 is continuous within the limits of accuracy of the measurements. Slight irregularities could be noticed in the experiments run in the presence of gases (figure 2); however, these are not shown in the figure.

In the second series (also adsorption of water on silica gel) the effect of air, hydrogen, nitrogen, and oxygen at higher pressures is examined. As is shown in figure 2, the rate of adsorption—at 4.6 mm. of water vapor and 25°C.—in gases of similar molecular weight (oxygen, nitrogen, air) is dependent only on the pressure and increases rapidly as the pressure decreases. Further, the rate of adsorption in a gas of low molecular weight, such as hydrogen, is much greater than in a heavier gas at the same pressure. Almost all of the points measured fall, within the experimental limit of error, on the curves given. However, particularly at high values of t , some of the points deviated considerably because of the changes of pressure of the permanent gas resulting from the solution of the gas in water. For example, at the start of several experiments the water was gas-free; as the experiments progressed the solution of the gas in the water caused a decrease in the pressure of the gas. These changes amounted in some cases to almost 25 per cent of the total pressure of gas. Experiments (not shown in figure 2) were performed in the presence of hydrogen at 1.1 mm., and oxygen at 3.0 mm. As was to be expected, the former curve lies between curves 1 and 2 (figure 2) and the latter curve between 3 and 4.

We see from figure 1 that the rate of adsorption is independent of the presence of permanent gases when the pressure of the gas is low compared with the pressure of water vapor. From figure 2 we see that at higher pressures the rate depends on both the molecular weight and the pressure of the inert gas. These facts led us to believe that the difficulty of diffusion of the water vapor through the inert atmosphere may alone be sufficient explanation for the behavior of the rate of sorption. In addition, other experiments show that there was no "soaking in effect", i.e., adsorption rates were independent of the length of time the dry gel was allowed to remain in the permanent gas. This, of course, implies that the gas has no specific effect or else the effect is instantaneous. By a specific effect we mean an effect which would slow down the rate of sorption by other means than mere physical hindrance to diffusion of the water vapor. For example, the gas itself might be adsorbed and this might prevent the water from wetting the walls of the gel. The rate of reaching equilibrium would then depend on the rather slow rate of displacement of the adsorbed gas by the water.

The results of series 3—desorption of water from silica gel, figure 3—offer additional evidence in support of the above view. The rate of desorption was measured by connecting the pumps with the tube containing the gel (saturated with water at 4.6 mm.), and measuring the amount of water lost by the gel at definite time intervals. Obviously, gases present in the vapor phase are immediately swept out, and—provided the sorption rate is not dependent on a specific effect—the rate of desorption should be independent of the nature and pressure of the gas present during the previous

adsorption. Figure 3 shows this to be, for the most part, the case. However, one interesting exception appears; namely, that the difficulty of

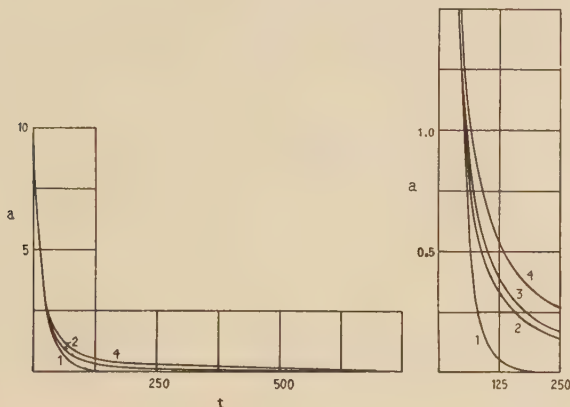


FIG. 3. Desorption from silica gel. Ordinate: a in grams per 100 grams of dry gel. Abscissa: time, t , in minutes. Temperature of gel, 25°C . Desorption followed establishing equilibrium between the gel and water at 4.6 mm. pressure. Curve 1, the pressure of air in the apparatus during the preceding adsorption was 4×10^{-4} mm. Curve 2, the gas present was air, nitrogen, or oxygen at 1 mm. pressure. Curve 3, hydrogen at 3 mm. Curve 4, air, nitrogen, or oxygen at 3.5 mm.

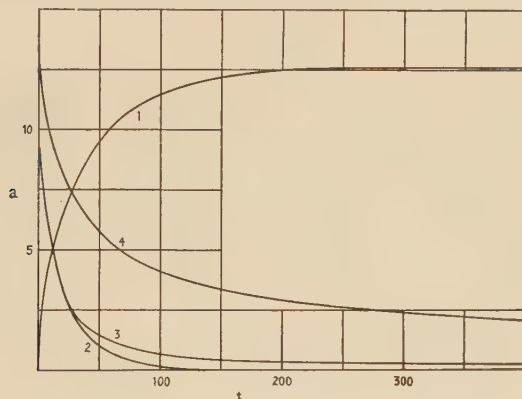


FIG. 4. Adsorption and desorption on iron-silica gel. Ordinate: a in grams per 100 grams of dry gel. Abscissa: time, t , in minutes. Pressure of water vapor, 4.6 mm. Temperature of gel, 25°C . Curve 1, adsorption rate on iron-silica gel in the absence of gases (pressure of gas = 2×10^{-4} mm.). Curve 4, desorption following adsorption in curve 1. Curves 2 and 3 are copied from curves 1 and 4, respectively, of figure 3.

desorbing the last few per cent of the sorbed water (see figure 3, inset) is indeed dependent on both the nature and pressure of the gas present in the

apparatus during the preceding adsorption. It is possible that the gas⁴ trapped in the capillaries of the gel hinders the desorption of the water, again, merely by physical resistance to diffusion of the water vapor. This hypothesis is supported by the fact that the rate of desorption of the last bit of water is greater in hydrogen—small molecular weight—than in air, oxygen, or nitrogen.

If the above hypothesis is correct, the results of the experiments with the iron-silica gel (figure 4) are particularly interesting. Even following adsorption in a good vacuum (curve 1), the rate of desorption (curve 4) of the last 3 per cent of the water is extremely slow. In fact, we see from figure 4 that curve 4 corresponds more closely to curve 3—desorption from silica gel in the presence of oxygen, nitrogen, or air (at 3.6 mm.)—than to curve 2—desorption from silica gel *in vacuo*. This might well indicate the presence in the pores of this gel of a trace of gas⁵ which cannot be eliminated by activation but which is sufficient to hinder the desorption of water.

Of interest in connection with the peculiarities of the iron-silica gel is the work of Lambert and Clark (9), who found that the adsorption of benzene on ferric oxide gel gave an entirely different type of isothermal than the adsorption of benzene on silica gel.⁶ Subsequently the same investigators (10) found hysteresis in the sorption of benzene on ferric oxide gel, but no hysteresis with silica gel.

SUMMARY

1. At 25°C. and at a vapor pressure of water of 4.6 mm., two to three hours is sufficient to establish equilibrium between silica gel and water, provided the pressure of the permanent gas present is below 0.5 mm. That is, the rate of adsorption of water on silica gel is independent of the permanent gas present when the pressure of that gas is below 0.5 mm.

2. At higher pressures of gas the rate is an inverse function of the pressure and the molecular weight of the gas present. Thus at a given pressure the rate is most rapid in hydrogen.

3. The rate of desorption of the last part of the water to be pumped off is an inverse function of the pressure and molecular weight of the gas present during the previous adsorption. The desorption of the first and larger portion of water is quite independent of the gas present.

⁴ For example, the gas may have been adsorbed by the gel before or during the adsorption of water, or it may have dissolved in the sorbed water.

⁵ Presumably oxygen resulting from the decomposition of ferric oxide. Mellor (12) quotes Sossman and Hostetter to the effect that the decomposition of ferric oxide is measurable as low as 100°C.

⁶ Plotting pressure as abscissa and amount sorbed as ordinate, the silica gel gave a curve roughly parabolic; the ferric oxide gave a sigmoid curve.

4. The rate of desorption from an iron-silica gel, following adsorption *in vacuo*, is much less than in the case of silica gel, and is similar to the rate of desorption for silica gel following adsorption in the presence of a gas.

5. All the observed facts may be qualitatively accounted for on the basis of the resistance of an inert gas to diffusion of water vapor, both in the vapor phase around the gel and in the pores of the gel.

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BIOGRAPHY

The author of this dissertation was born in Baltimore, Md., on September 23, 1913. He received his early education in the elementary schools of this city and in the Baltimore City College. In October 1930 he entered the Johns Hopkins University, and received the degree of Bachelor of Arts in June 1932. In October 1932 he was admitted to the School of Higher Studies of the Faculty of Philosophy as a graduate student in Chemistry.

